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Solubility and Polarity

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SOLUBILITY AND POLARITY

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Since the phenomenon of solubility is one of such common occurrence and universal familiarity, it is no wonder that a great many attempts have been made to learn the cause of it. The molecular weight of solute and solvent, the dielectric constants, the size of the molecules concerned, the surface tensions of the components, adsorption, the vapor pressure above the solution, the magnitude of Van der Waal's a and b for the components, their internal pressures as determined by a great many different methods — all these and many other avenues of approach have been used, only to be discarded again because they did not lead to a solution of the problem. Combinations of some of these factors also have been investigated in the hope that solubility might be found to depend jointly on several of these characteristics.

In 1885, Van't Hoff determined the relation existing between osmotic pressure and the amount of solute in solution. About the same time Arrhenius established a relation between electrolytic dissociation and the conductivity of an electrolyte. Two years later Raoult conducted a series of experiments which led him to establish what is known as Raoult's Law for vapor pressure, thereby connecting the amount of solute in solution with the lowering of the vapor pressure above a solution as more and more solute is added. Since that time many efforts have been made with this work as basis, to determine the cause of solubility. What property of the molecule is brought into play as it dissolves among other molecules? What forces are brought to bear upon solute and solvent in the act of solution? Are these forces always the same? And what has molecular structure to do with the process of solution?

INTERNAL PRESSURE

The method of attack upon which most stress has been laid in recent years is that of Dr. Hildebrand [1] who has relied on internal pressure as the main factor in the determination of solubility, stating that when two components have equal or nearly equal in-

[1] Hildebrand, Jour. of Amer. Chem. Society, Vol. 38, p. 1452 (1916).

ternal pressures, then they will be soluble in each other in all proportions. In other words, when a molecule of solute is under the same forces when surrounded by molecules of its own kind as when it is surrounded by molecules of solvent, then solution will take place; but when these forces are altogether different, solubility will not take place. Thus he explains the immiscibility of benzene in water as being due to the great difference in the internal pressure between the two components. The miscibility of alcohol and water, he claims, is due to the similarity of the internal pressures of the two liquids but is influenced also by their polarity.

The internal pressure of any component can be determined by three or four different methods and while concordant results are not obtained, the order of arrangement is in general the same. Hildebrand has the support of Bradford who comes to the same conclusion, although his mode of approach is somewhat different.[2]

When, however, we note a number of cases, no such universal agreement as these men claim between solubility and internal pressure seems to occur, for illustrations can be found where two components have nearly the same internal pressure and yet are not soluble in each other. Again components can be found which are miscible in all proportions but their internal pressures are by no means alike. Such cases are not in harmony with the theory and hence we can not depend on this principle to solve the problem of solubility.[3]

POLARITY

Let us now consider the effect of polarity on solubility. By polarity we mean the condition or state of being polar, i.e. the molecules of a substance have the same property as magnets in the sense that they can attract other molecules of like properties. Thus if we have a polar substance, its molecules will attract each other and association will take place.

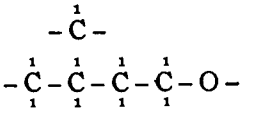
In Table I are given the solubilities in ccs. of CO_2 per cc. of the solvent listed. The results in Tables I, II, and III are due to Just [4] and were taken at 20° C. The chemical formulæ and the structural formulæ of the solvents also are given. For simplicity the H's are omitted in the structural formulæ.

2 Bradford, Phil. Mag. 38, p. 696 (1919).
3 For a further discussion of this and related theories of solubility the reader should consult Phys. Rev. May, 1922.
4 Just, Zeit. für Phys. Chem. 37, p. 342 (1901).

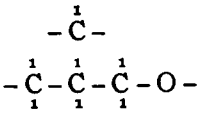
TABLE I

Sol. in ccs.

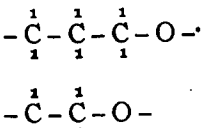
1.83 Isoamyl Alcohol — $C_5H_{11}OH$ —



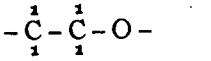
1.85 Isobutyl Alcohol — C_4H_9OH —



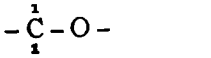
2.49 Propyl Alcohol — C_3H_7OH —



2.70 Ethyl Alcohol — C_2H_5OH —



3.83 Methyl Alcohol — CH_3OH —



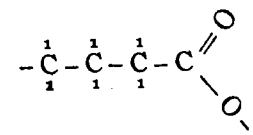
It may be noted here that the solubility of CO_2 in these alcohols increases as their association or polarity factor increases, for it is generally known that polarity increases as we go down the column. CO_2 is considered a polar substance and it is here shown to be more soluble in polar solvents than in non-polar solvents. The first two alcohols above tabulated are iso-compounds and hence decidedly non-polar, and it will be noticed that the solubility of CO_2 in them is low.

In Table II we have a similar list leading to the same conclusion.

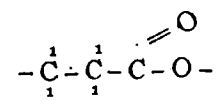
TABLE II

Sol. in ccs.

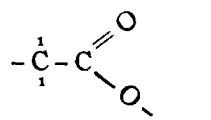
3.47 Butyric Acid — $C_4H_8O_2$ —



4.07 Propionic Acid — $C_3H_6O_2$ —



4.67 Acetic Acid — $C_2H_4O_2$ —

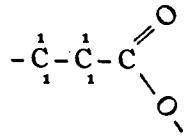


These solvents are somewhat similar in structure but we know that acetic acid is strongly polar and we also note that CO_2 is more soluble in it than in either of the other two solvents.

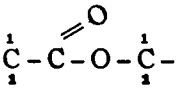
In the case of Propionic acid ($C_3H_6O_2$) and Methyl acetate ($C_3H_6O_2$) (two substances having identical molecular weight) we

find that CO_2 has a solubility of 4.07 ccs. in the former and of 6.49 ccs. in the latter. This difference seems to be due to the greater polarity of Methyl acetate as shown by the structural formula, which gives to Methyl acetate greater symmetry and hence greater polarity.

Propionic acid —



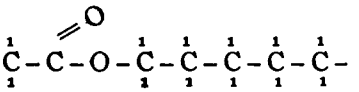
Methyl acetate —



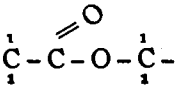
CO_2 is more soluble in Amyl chloride than in Amyl bromide, more in Ethylene chloride than in Ethylene bromide, and more in Chloro benzene than in Bromo benzene — all because the chlorides are more polar according to their structure than are the bromides.

TABLE III

4.12 Amyl acetate — $CH_3COOC_5H_{11}$ —

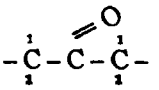


6.49 Methyl acetate — CH_3COOCH_3 —

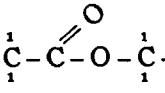


In Table III the first column represents the solubility of CO_2 in the solvent shown in the second column. Both solvents are polar but Methyl acetate has its poles closer together and hence is more strongly polar. CO_2 is more soluble in it than in Amyl acetate and this is as it should be according to this theory.

Ortho-toluidine and meta-toluidine have very nearly the same structure. They should therefore show approximately the same solubility. For the former 1.38 ccs. represents the solubility, and for the latter 1.43 ccs. of CO_2. This is in accord with the theory. Again, the solubility of CO_2 in Acetone (CH_3COCH_3) —



is 6.29 ccs. and in Methyl acetate (CH_3COOCH_3) —



it is 6.49 ccs. Both of these solvents are strongly polar and their structures are very nearly alike. We should therefore, expect the solubilities to be about the same, and both should be high.

TABLE IV

Solvent	Solubility at 20° of CO_2 A	of N_2O B	Ratio $\frac{A}{B}$
Water	0.9000	0.675	1.335
Acetone	6.98	6.03	1.155
Acetic Acid	5.23	4.85	1.078
Pyridine	3.85	3.58	1.075
Methyl Alcohol	3.57	3.32	1.07
Ethyl Alcohol	2.87	2.99	0.96
Benzaldehyde	2.98	3.15	0.95
Aniline	1.38	1.48	0.94
Amyl Acetate	4.65	5.14	0.905
Ethylene Bromide	2.27	2.81	0.808
Isoamyl Alcohol	1.91	2.47	0.773
Chloroform	3.71	5.60	0.664

In Table IV are listed the solubilities of CO_2 and N_2O in twelve different solvents as obtained by the writer. In the last column are given the ratios of the solubility of CO_2 to that of N_2O in any one solvent. N_2O is considered less polar than CO_2, and should therefore be found less soluble in polar solvents and more soluble in non-polar solvents than CO_2. Table IV bears out that contention, for those solvents which are near the top are generally considered polar while those near the bottom of the table are non-polar. This means that the ratio of the solubility of CO_2 to that of N_2O should be greater than one near the top and less than one near the bottom, as it is actually found to be.

While this theory does not pretend to explain the entire problem of solubility, it points out a method of approach which it seems has not been sufficiently emphasized thus far.

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